

Thiophosphate Based Super-ionic Conductors and Cathodes

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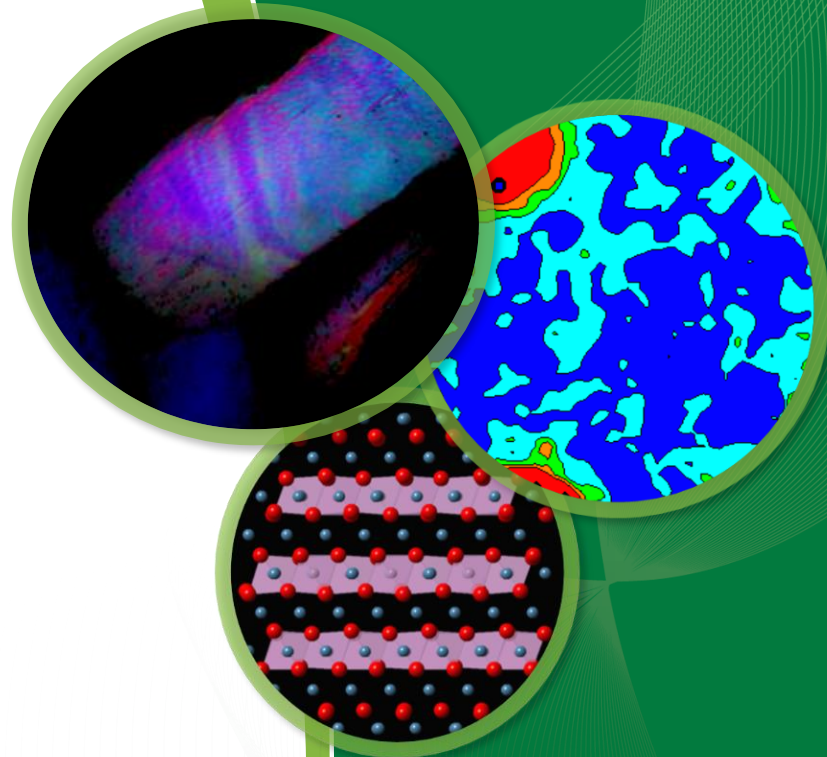
**2018 U.S. DOE Vehicle Technologies Office
Annual Merit Review**

June 12th, 2019

Project ID: BAT422

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Overview

Timeline

- Project start date: Oct. 1, 2018
- Project end date: Sept. 30, 2021
- Percent complete: 30

Budget

- FY19 Funding: \$ 400K

Barriers

Performance: (i) Cell energy density, 500 Wh/Kg -1000 cycles (ii) Stable ionic conductivity $> 10^{-4}$ S/cm at room temperature

Interfacial Stability: Chemical and electrochemical stability 0 – 4.5 V wrt Li^0/Li^+

Current Density : 2 mA/cm² or higher

Partners/Collaborators

- *Pacific Northwest National Laboratory*
Electron Microscopy
- *SLAC - SSRL*
Synchrotron X-ray diffraction, XANES
- Prof. Steve Greenbaum
Hunter's College, New York
NMR Studies

Impact

Relevance

High lithium-ion conducting solid electrolytes with stable interfaces are critical to the development of all solid state batteries that meets EV goals in terms of energy density and life.

Objectives

- Synthesis and fabrication of lithium thiophosphate based superionic conductors and evaluate their electrochemical and chemical stability.
- Synthesis of high capacity cathodes based on **sulfur catenation** to a solid polymeric thiophosphates ionic conducting framework.
- **Cathode-Solid Electrolyte Interfaces :**
 - (i) Optimizing and reduce the area specific resistance (ASR) between thiophosphate solid electrolyte (SE) and a working lithium-ion cathode (**soft-hard interface**).
 - (ii) Meet the electrochemical stability and critical current density goals for all solid-state batteries

Relevance to VTO Mission

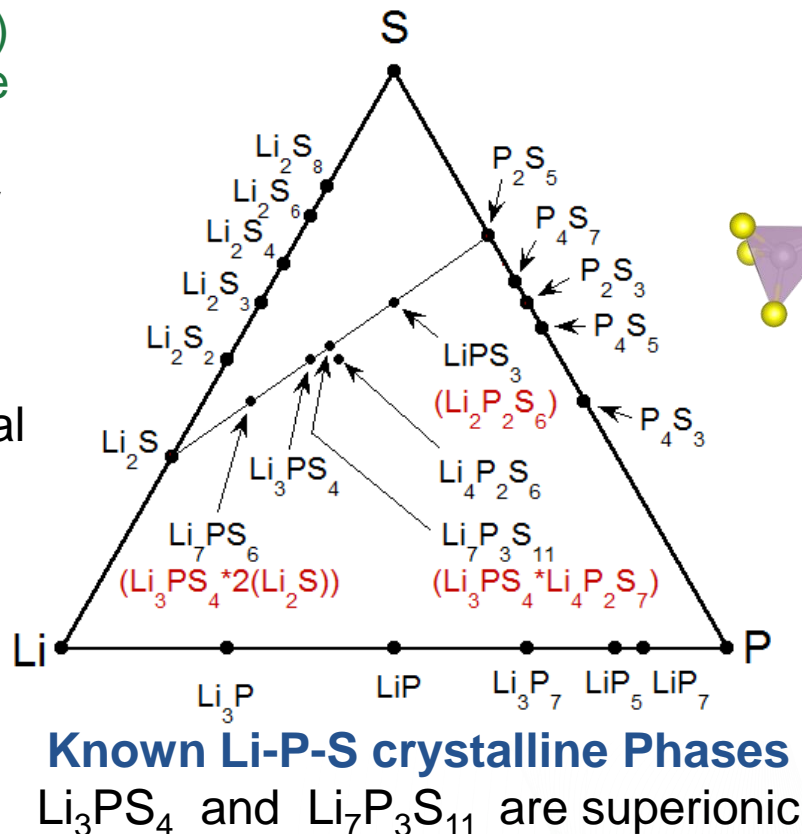
R&D effort on solid state electrolytes and interfaces are critical to meet the VTO's long term goal of attaining cell energy density ≥ 500 Wh/Kg and 1000 EV cycles.

Milestones

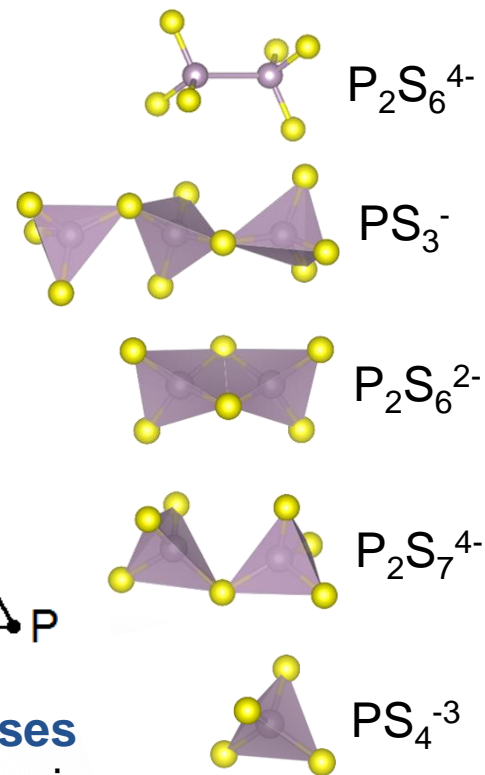
Due Date	Description	Status
12/31/2018 (Q1)	Undertake synthesis and structural characterization of two lithium thiophosphate and related class of superionic conductors based on Li-P-S phase diagram.	Complete
03/31/2019 (Q2)	Attain lithium-ion conductivity in the range of 10^{-4} S/cm at room temperature by optimizing the synthesis method, dopant concentration and surface properties.	Complete
06/30/2019 (Q3)	Complete characterization and evaluation of the reaction passivation layer at Li-metal interface by undertaking AC impedance and DC polarization test in symmetric cells.	In progress
09/30/2019 (Q4)	Complete characterization and evaluation of the reaction passivation layer at cathode interfaces by undertaking AC impedance and DC polarization test in symmetric cells as well as Li-ion cathodes.	In progress

Lithium thiophosphate (Li-P-S) class of solid electrolytes have certain unique advantages

- Superionic ion conductivity ($> 10^{-4}$ S/cm) at room temperature
- Mechanically Soft : Good wettability with lithium metal and processable
- Earth abundant and potentially lower cost



Approach/Strategy

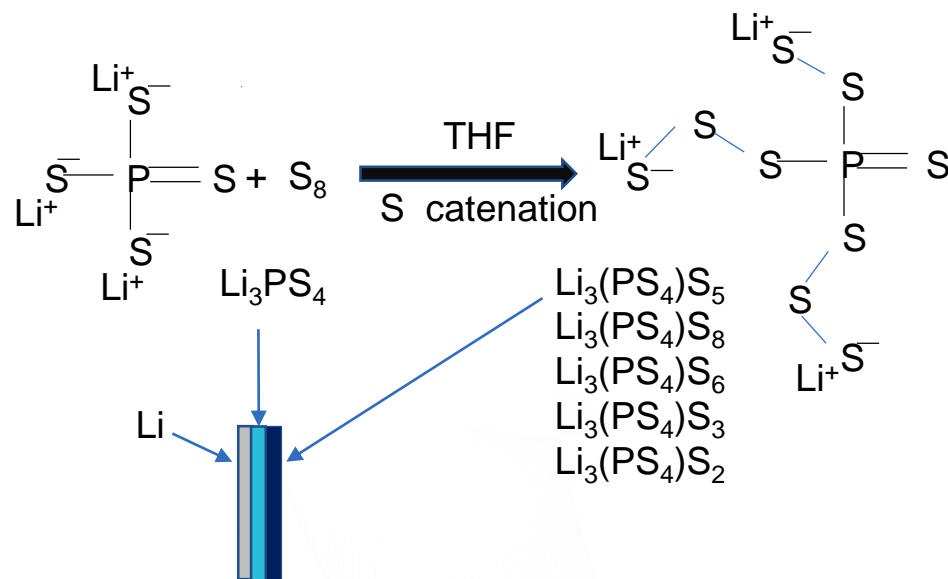
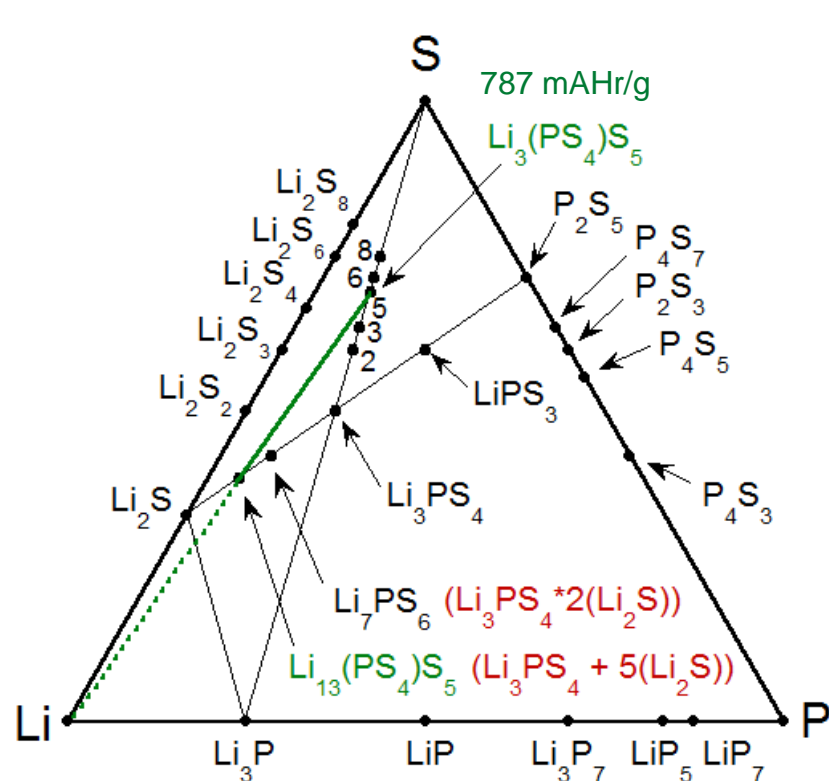


Most of the three-component compounds are on the $\text{Li}_2\text{S} - \text{P}_2\text{S}_5$ tie-line with P^{+5} oxidation state, P is coordinated to S as isolated tetrahedra or with edge or corner sharing tetrahedra

Li_7PS_6 and $\text{Li}_7\text{P}_3\text{S}_{11}$ can be written as $\text{Li}_3\text{PS}_4 \cdot 2(\text{Li}_2\text{S})$ and $\text{Li}_3\text{PS}_4 \cdot \text{Li}_4\text{P}_2\text{S}_7$ to emphasize phosphorus coordination and stoichiometric relations. These notations do not denote mixtures of two phases.

Prior ORNL work demonstrated high capacity cathodes by catenation of sulfur on to thiophosphate phases as described by the phase diagram

Catenation of 2, 3, 5, 6 and 8 sulfur atoms onto Li_3PS_4 electrolyte^[1-2]



Solid State Cell
 ~2.4 V, 300 cycles, 60 °C
 550 mAh/g($\text{Li}_3(\text{PS}_4)\text{S}_5$)

- Only the catenated sulfur is electrochemically active
- Capacity and cycle life limited by Li_2S formed during discharge

^[1] Lin, Liu, Fu, Dudney, Liang, Angew. Chem. 2013, 125, 7608-7611.

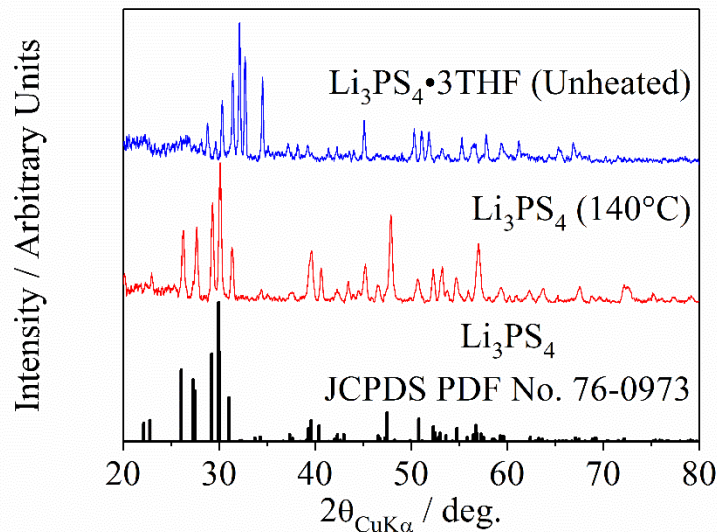
^[2] Liang, Dudney, Lin, Liu, US Patent No. 9,466,834 B2, 2016.

A model thiophosphate solid electrolyte (Li_3PS_4 , LPS) was prepared using a solution-based synthesis route

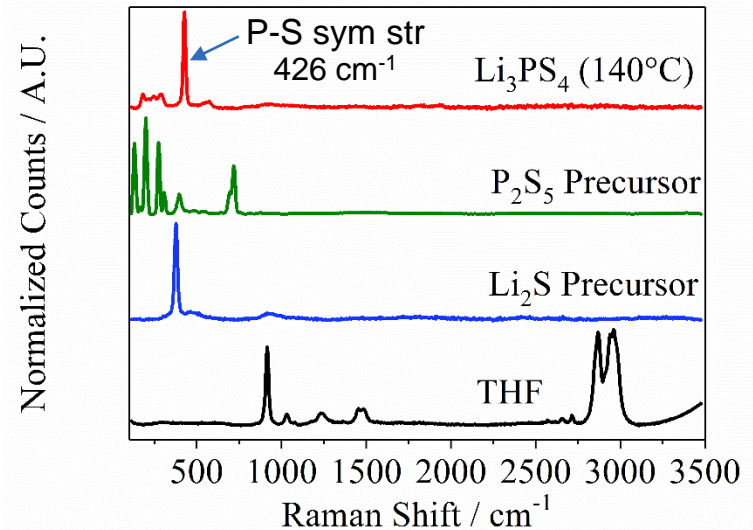
Synthesis Details:

- Ball-mill $\text{Li}_2\text{S} + \text{P}_2\text{S}_5$ in THF
- Centrifuge and decant supernatant
- Dry Li_3PS_4 solid at 140°C under vacuum
- All work performed under argon

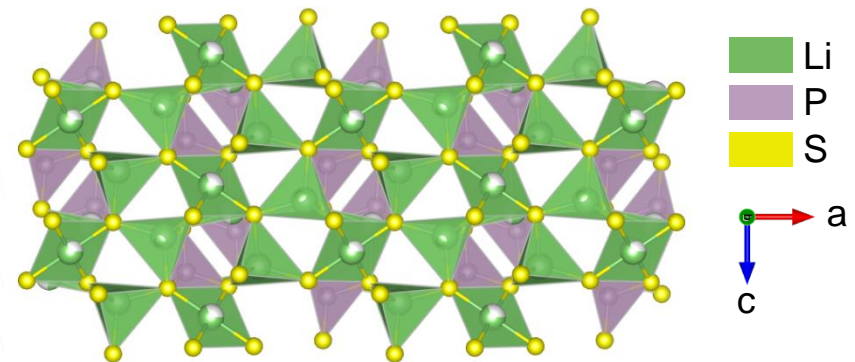
XRD



Raman



Li_3PS_4 Structure

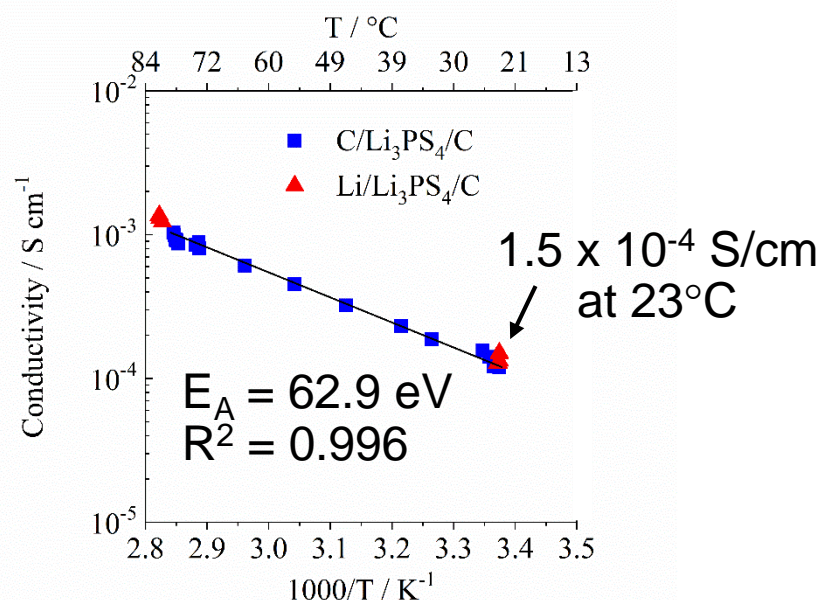
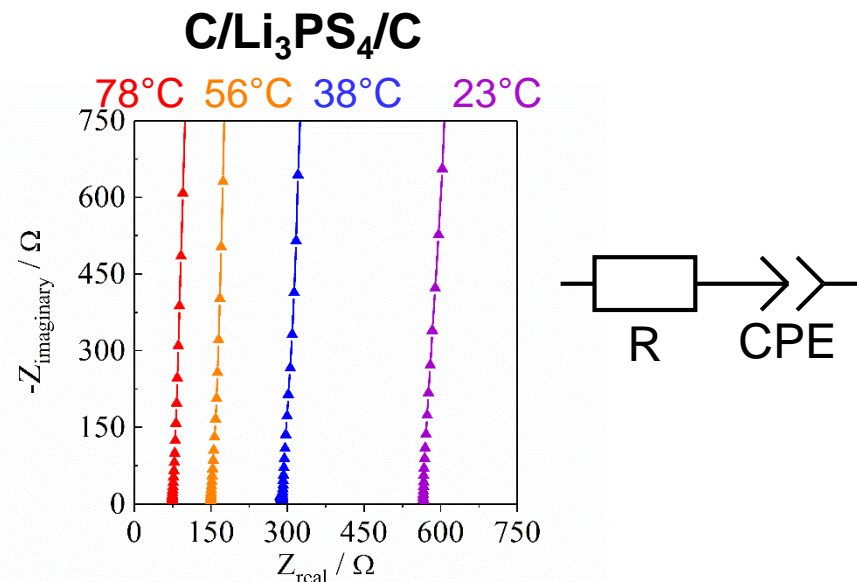
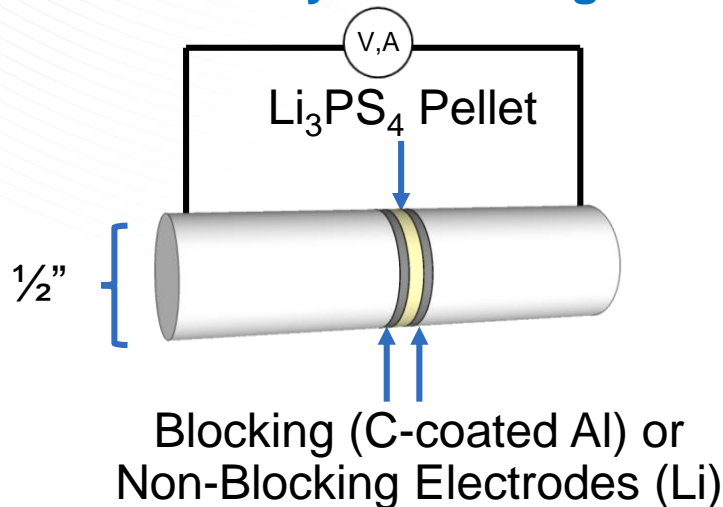


1. Li_3PS_4 with/without coordinated THF have different structures. Heating at 140°C removes coordinated THF

7 2. Li_3PS_4 product is phase-pure with no residual $\text{Li}_2\text{S}/\text{P}_2\text{S}_5$ precursors

Li_3PS_4 exhibits superionic Li^+ conductivity (e.g., $1.5 \times 10^{-4} \text{ S/cm}$ at 23°C) as determined from both blocking and non-blocking electrode configurations.

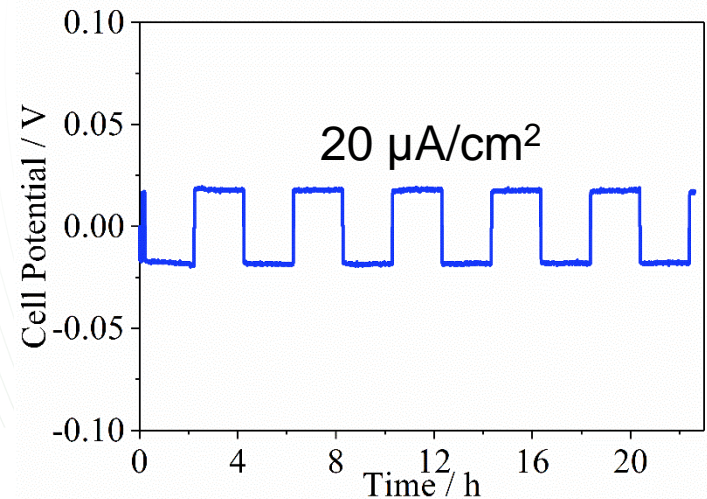
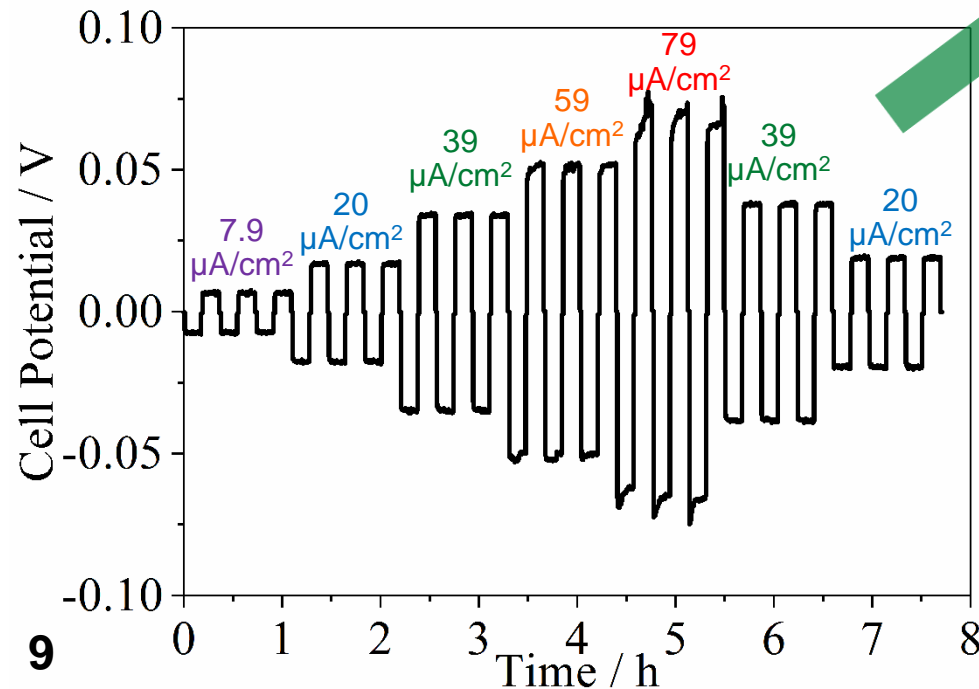
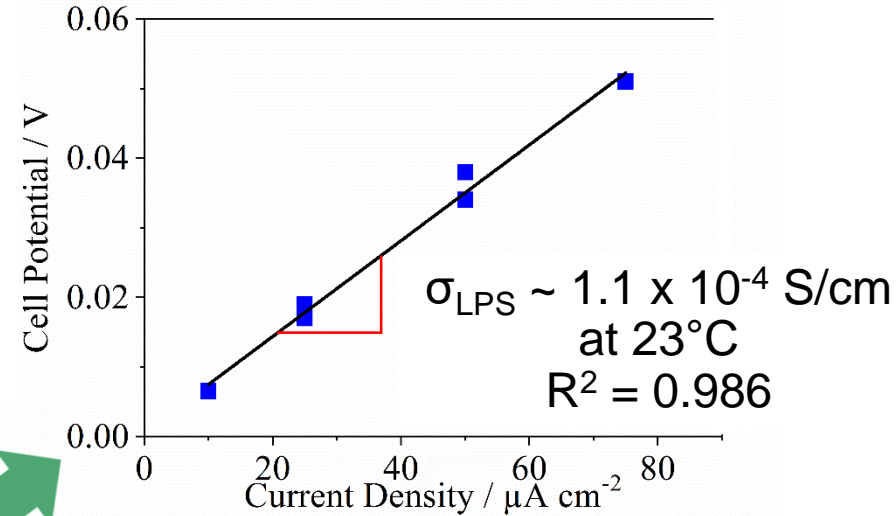
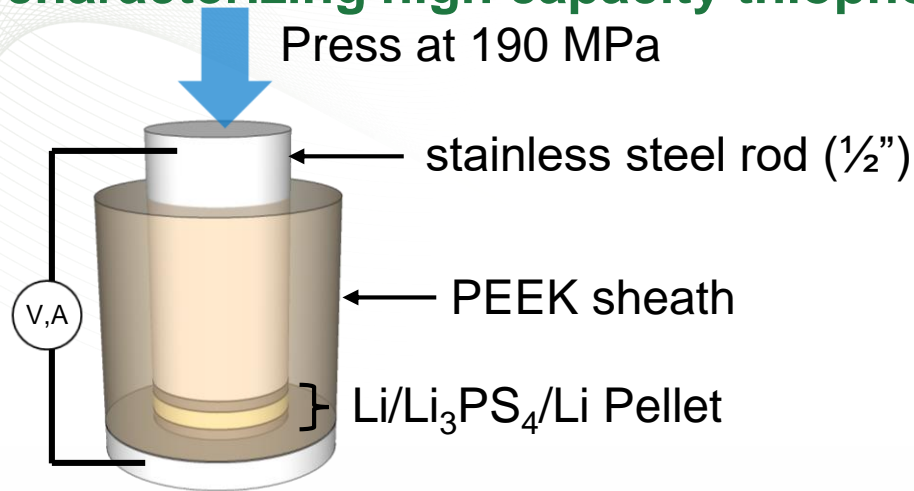
Conductivity Cell Configuration



Pressure (MPa)	Pellet Density (g/cm^3)	Relative Density*
190	1.29	0.69
380	1.60	0.86
560	1.65	0.88

* Calculated from theoretical density of Li_3PS_4 (1.87 g/cm^3)

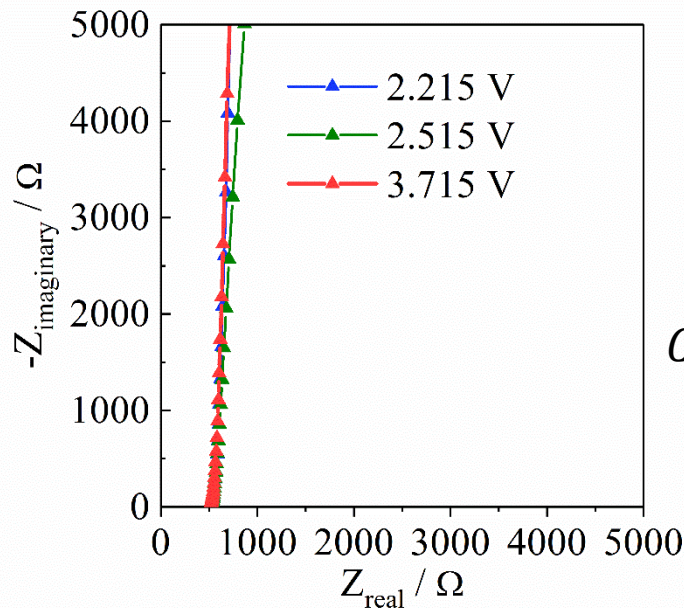
A Li/Li₃PS₄/Li solid-state cell was designed and tested to identify appropriate current densities and areal capacities to be used for characterizing high capacity thiophosphate cathodes.



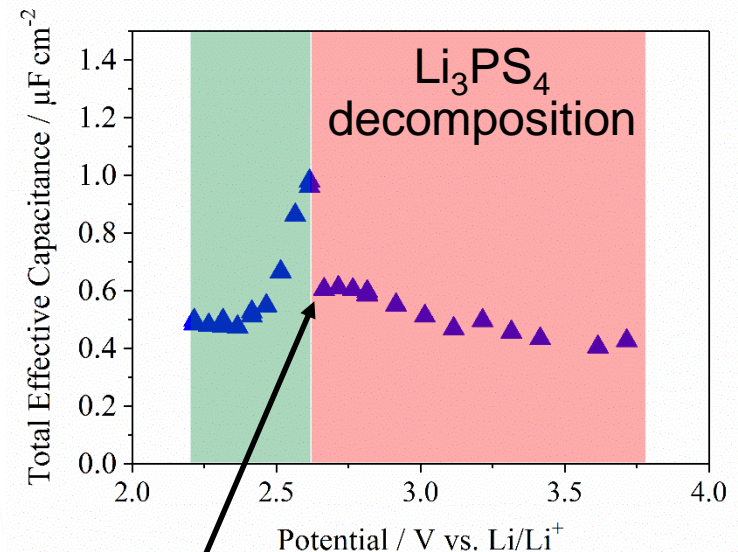
AC impedance measurements indicate Li_3PS_4 oxidizes at potentials > 2.6 V vs. Li/Li^+ . Stable cathode/electrolyte interfaces are critical for all-solid-state batteries.

Experimental Details

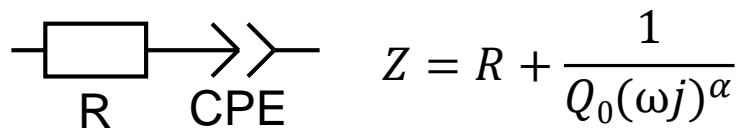
- **Asymmetric Cell:** $\text{Li}/\text{Li}_3\text{PS}_4/\text{C}$ ($E_{\text{oc}} = 2.21$ V)
- Polarize C electrode ($2.21 - 3.71$ V vs. Li/Li^+) and measure AC impedance



$$C_{\text{effective}} = Q_0 \frac{1}{\alpha} R^{\frac{1-\alpha}{\alpha}}$$



Measured decomposition potential (2.6V) in excellent agreement with recent modeling and experimental reports^[1-2]



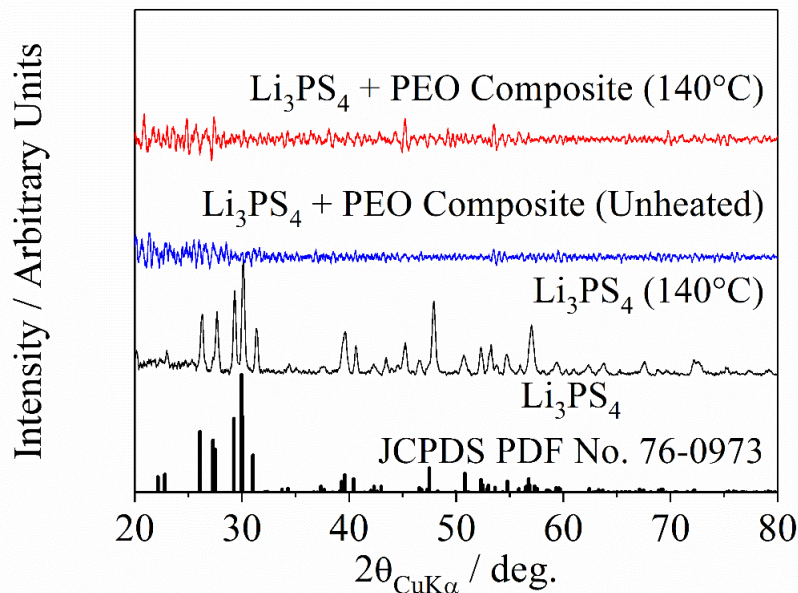
[1] W. D. Richards et al. Chem. Mater. 2016, 28, 266-273.

[2] T. Hakari et al. J. Power Sources 2015, 293, 721-725.

A new synthesis route to produce PEO/Li₃PS₄ composite solid electrolytes was explored. Further optimization of the composition and synthesis conditions is required to achieve suitable ionic conductivity.

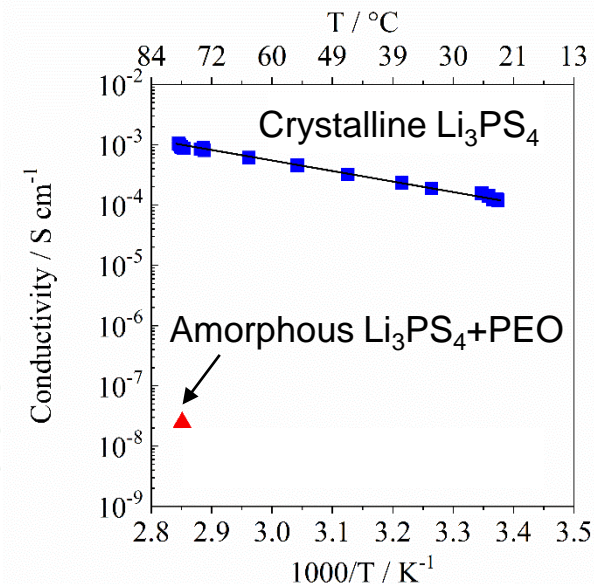
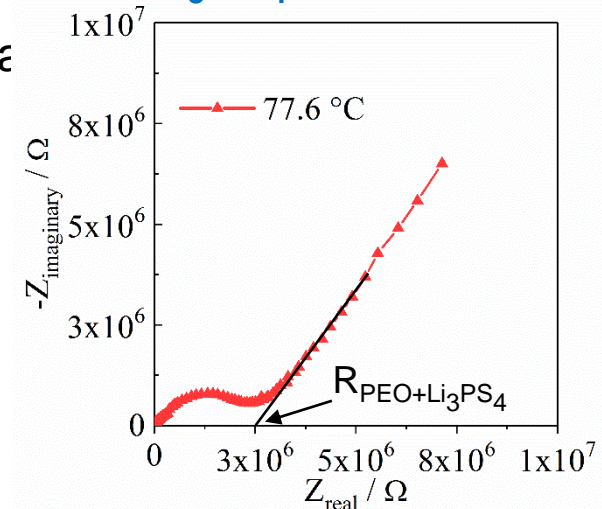
Li₃PS₄ + PEO Synthesis Details:

- Ball-mill Li₂S + P₂S₅ + polyethylene oxide (PEO, 600 kDa) in acetonitrile
- Centrifuge and decant supernatant
- Dry solid overnight at 25 – 140 °C
- All work performed under argon
- **Target composition: 56 wt% PEO, 44 wt% Li₃PS₄**



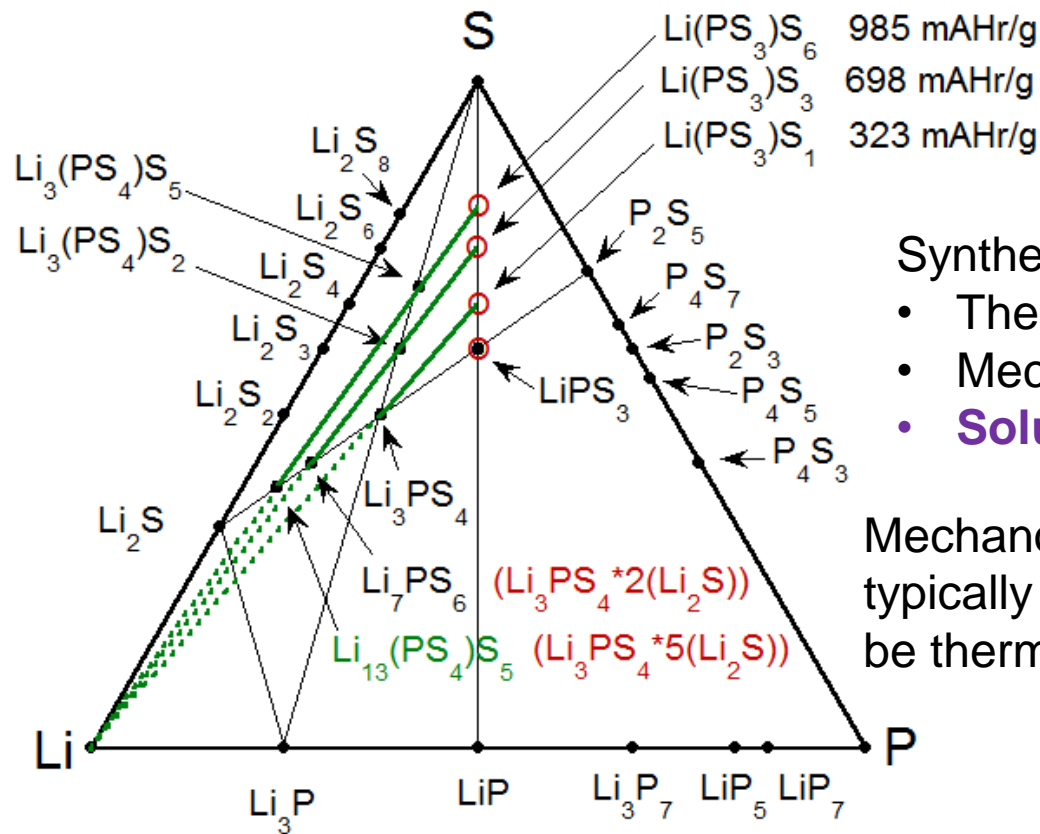
PEO matrix inhibits crystallization of Li₃PS₄ even at 140 °C

C/Li₃PS₄+PEO/C Cell



In our approach we propose catenation of S to $(\text{PS}_3)^{-1}$ to extend the capacity of the thiophosphate cathodes.

We have identified 3 new cathode compositions. $\text{Li}(\text{PS}_3)\text{S}_3$, $\text{Li}(\text{PS}_3)\text{S}_1$ are specifically chosen to ensure they don't form Li_2S during discharge which could lead to capacity degradation



→ New catenated sulfur cathodes

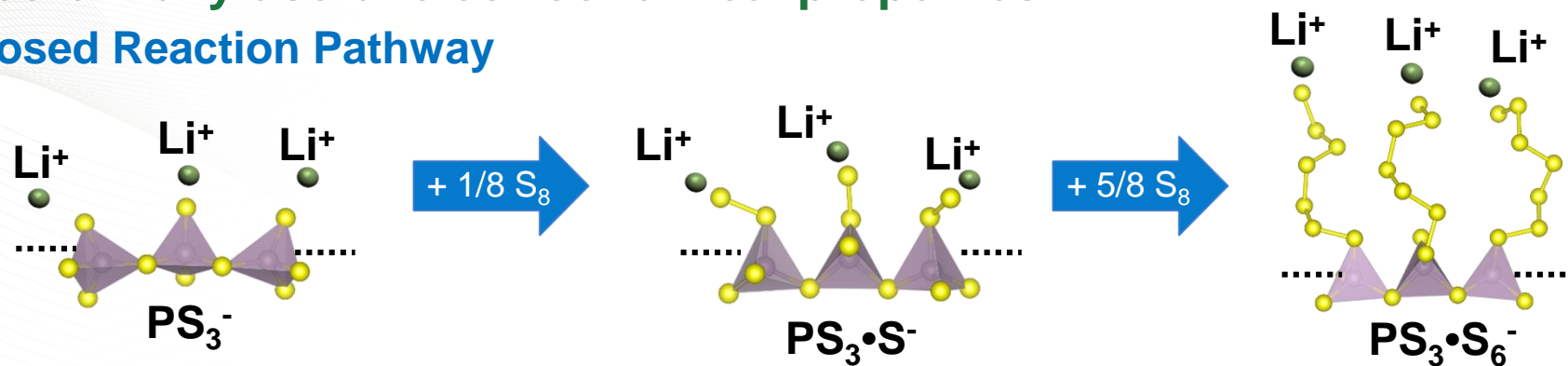
Synthesis method for thiophosphate SE

- Thermal
- Mechanochemical
- **Solution Precipitation – This work**

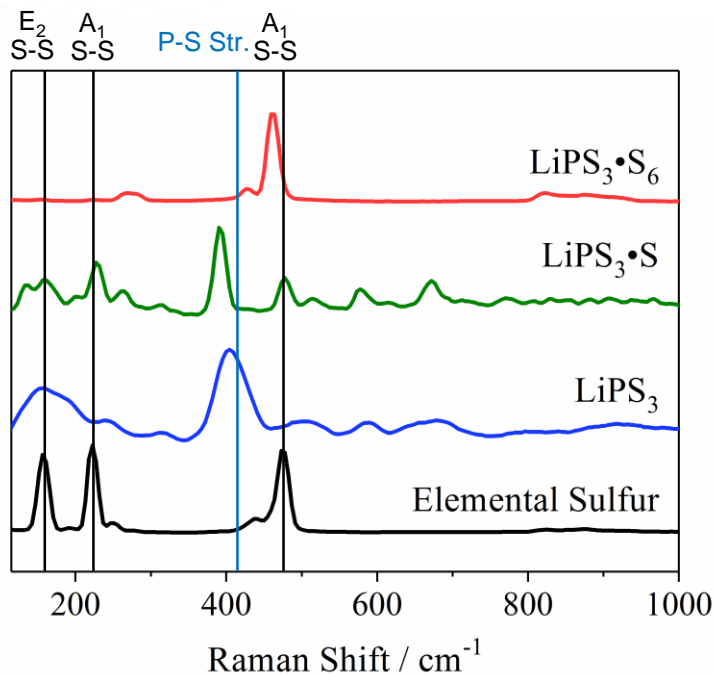
Mechanochemical and solution precipitation typically yield amorphous products that must be thermally annealed.

Sulfur can be catenated onto LiPS_3 to yield new crystalline thiophosphates with potentially useful electrochemical properties

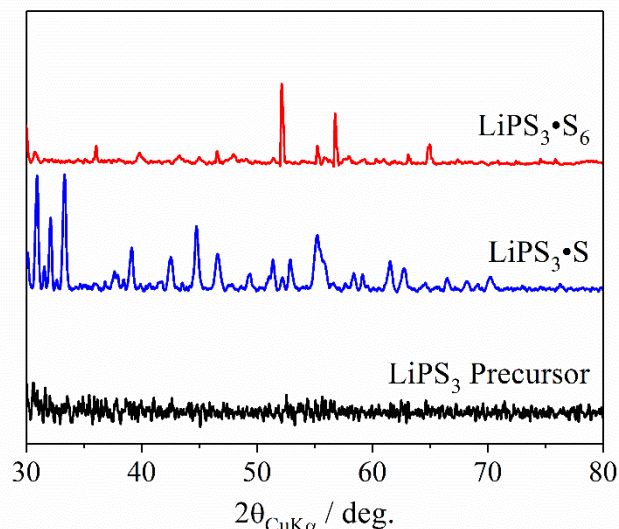
Proposed Reaction Pathway



Normalized Counts / A.U.



XRD

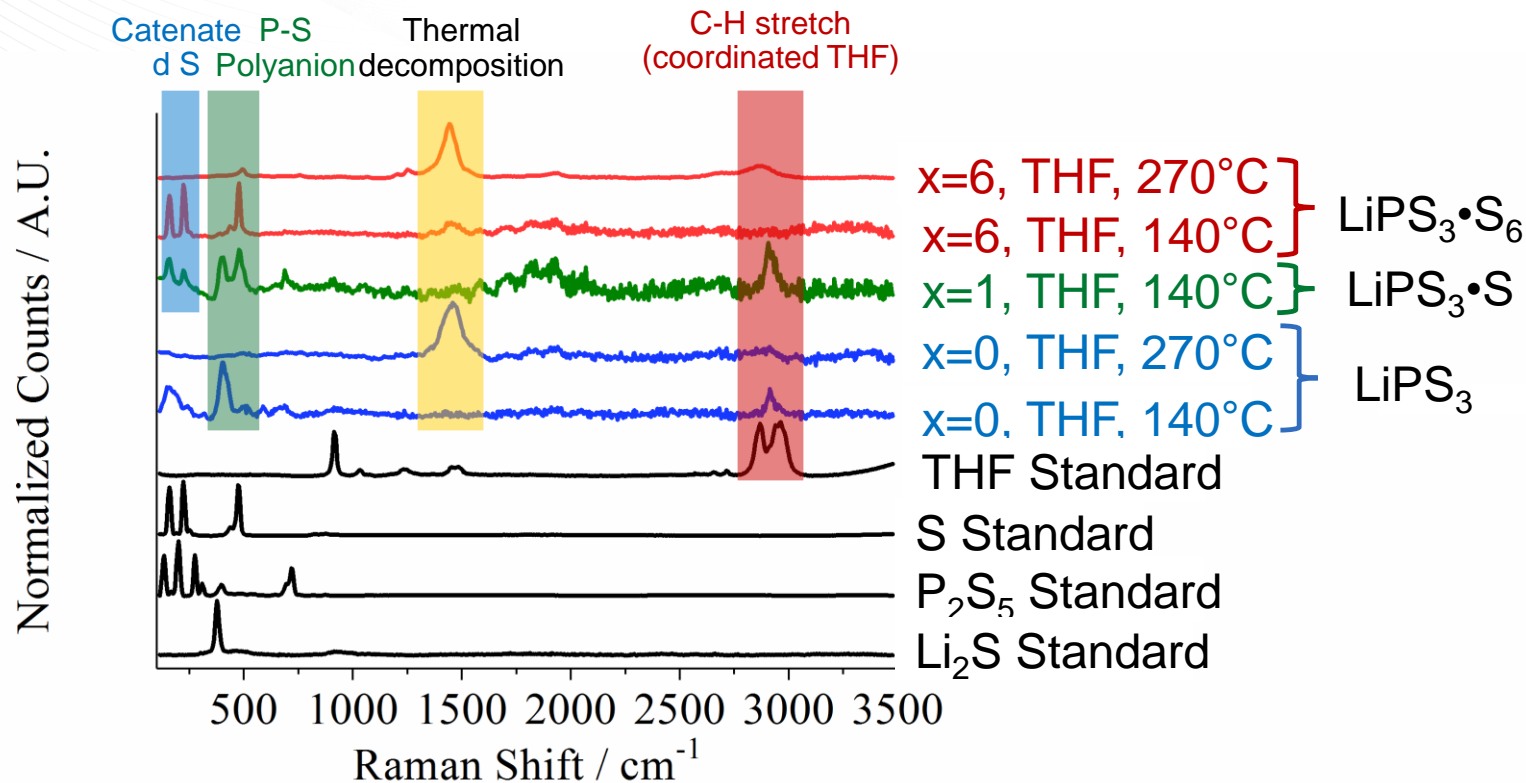


Diffraction peaks do not index with any known Li-P-S compounds

1. Catenating S onto LiPS_3 yields crystalline $\text{Li}_3\text{PS}_{3+x}$ compounds
2. Resulting structure is sensitive to thermal annealing conditions and solvent
3. In FY20, synchrotron XRD will be used to solve structure of new phases

Several amorphous $\text{LiPS}_3 \cdot \text{S}_x$ phases have also been prepared. Structural and electrochemical investigations of these new materials are underway.

Raman spectroscopy provides insights into structure of amorphous $\text{LiPS}_3 \cdot \text{S}_x$ compounds



1. Calcination temperature must be optimized for each composition to remove coordinated solvent without causing sulfur loss and/or thermal decomposition
2. Future work will investigate how glassy structure and coordinated solvent affect ionic conductivity.

Response to Reviewers Comments

New project started in FY 19 : Not reviewed

Collaborations and Coordination with Other Institutions



Electron Microscopy
Dr. Chongmin Wang



TXM-XANES and Soft X-ray Absorption
Dr. Yijin Liu and Johanna Weker



Nuclear Magnetic Resonance (NMR) Studies
Prof. Steve Greenbaum

Remaining Barriers and Challenges

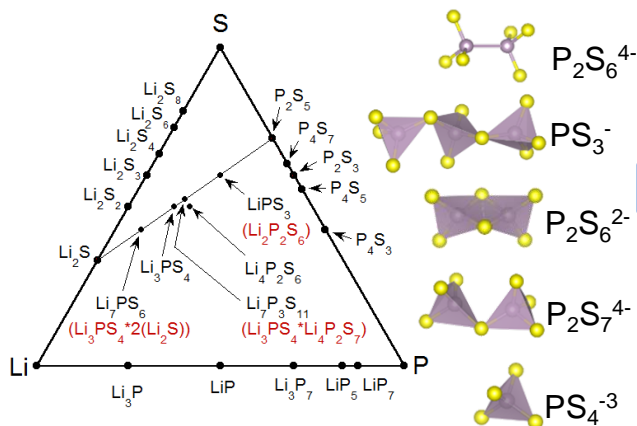
- Determine how sulfur catenation affects the ionic conductivity of LiPS_{3+x} phases.
- Establish optimal synthesis conditions (solvent, annealing time/temperature, etc.) to maximize the ionic conductivity of new Li-P-S phases.
- Determine how glassy structure and coordinated solvent affect ionic conductivity of amorphous Li-P-S phases.
- Reduce the interfacial resistance between the active material and ionically conductive medium (e.g., Li_3PS_4 or PEO+LiTFS) in composite cathodes for all-solid-state batteries
- Identify high energy density cathodes which form kinetically-stabilized interfaces with Li_3PS_4 (thermodynamically unstable at potentials > 2.6 V vs. Li/Li^+).

Any proposed future work is subject to change based on funding levels

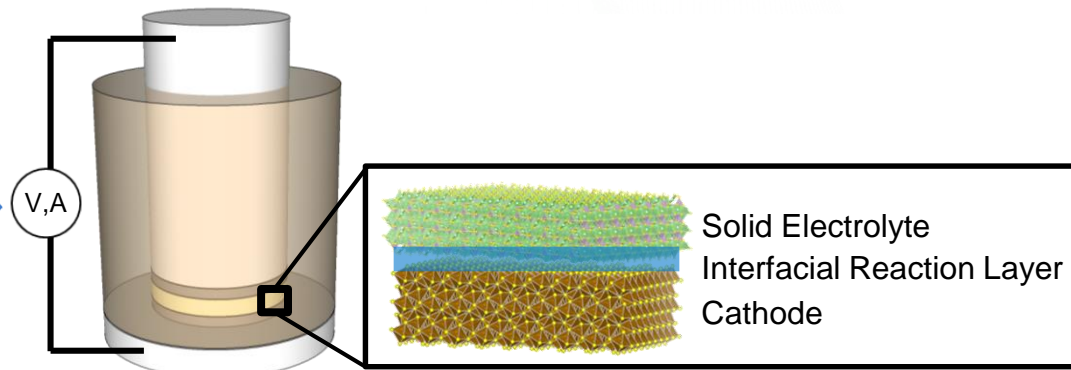
Proposed Future Research

1. Optimize the ionic conductivity and stability of lithium thiophosphate solid electrolytes. Specific experiments will incorporate: (i) **halide dopants** (e.g., I⁻) and/or (ii) barrier layers (e.g., LiNbO₃) to improve the ionic conductivity and interfacial stability of Li₃PS₄. FY19 3rd and 4th Qtr.
2. Establish structure-performance correlations for lithium thiophosphate solid electrolytes. Use neutron and synchrotron X-ray diffraction to solve the structure of new crystalline Li-P-S phases. Use neutron pair-distribution functions (PDF) to understand the local structure of amorphous, glassy phases. FY 20
3. Construct and test all-solid-state batteries containing superionic sulfide solid electrolytes and high energy density cathodes (e.g., S, FeS₂, and LiMO₂). Study the formation and stability of passive films formed at the cathode/electrolyte interface during battery operation. FY19 4th Qtr. and FY 2020

New Superionic Solid Electrolytes and Cathodes



Solid-State Batteries

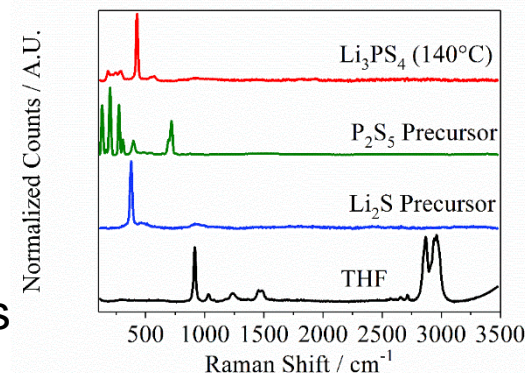


Summary

Technical Approach:

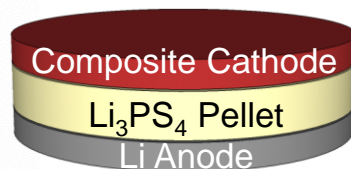
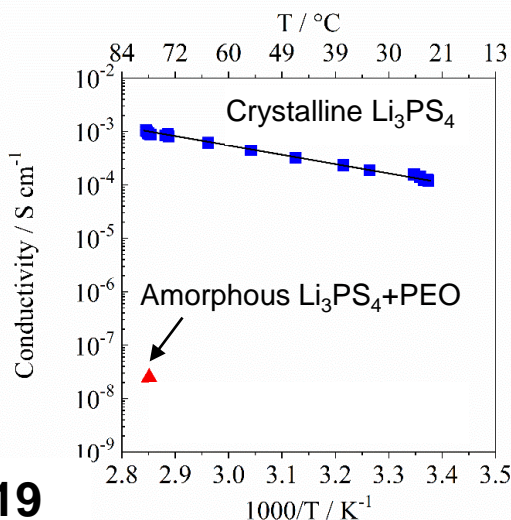
Catenate sulfur onto LiPS_3 to produce new crystalline and amorphous Li-P-S solid-state electrolytes and cathodes

- Targeted stoichiometries driven by ternary phase diagram
- Utilized a suite of characterization methods (e.g., XRD and Raman spectroscopy) to understand how synthesis conditions affect structure of Li-P-S phases



Accomplishments:

- Established a solution precipitation routes to synthesize a range of Li-P-S phases
- Synthesized a model sulfide electrolyte Li_3PS_4 with superionic conductivity ($1.5 \times 10^{-4} \text{ S/cm}$ at room temperature)
- Identified oxidative stability limit for Li_3PS_4 (2.6 V vs. Li/Li^+) using AC impedance spectroscopy



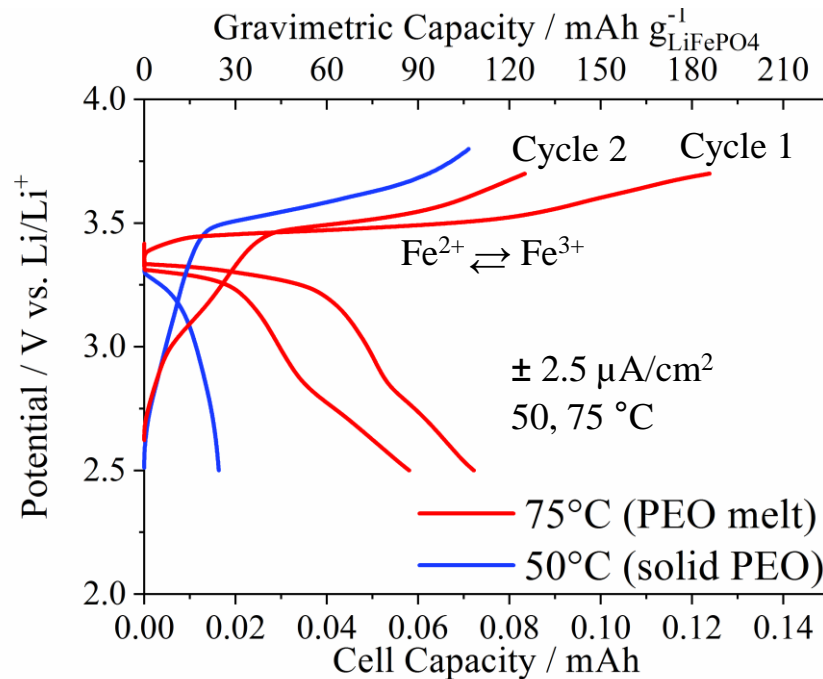
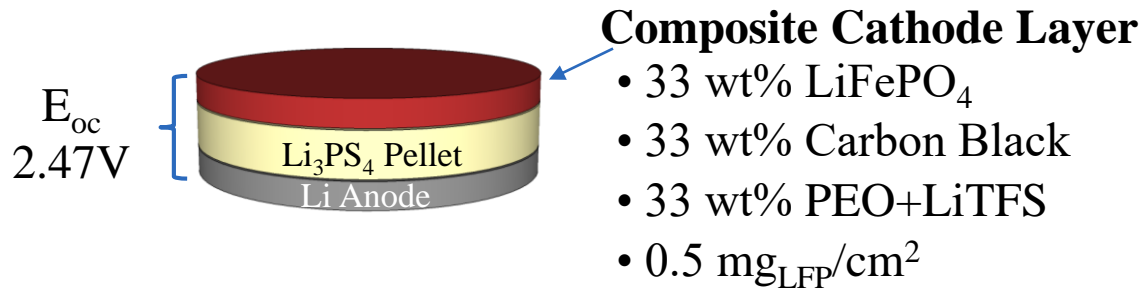
Ongoing work:

- Optimize synthesis and processing conditions for new Li-P-S phases
- Study cathode/electrolyte interfaces in all-solid-state batteries (e.g., $\text{Li/Li}_3\text{PS}_4/\text{LiFePO}_4$)
- Develop composite polymer/sulfide solid electrolytes to improve processability

Technical Back-up Slides

Preliminary experiments on all-solid-state Li/Li₃PS₄/LiFePO₄ batteries indicate performance is limited by cathode/electrolyte interfacial contact. Future work will focus on optimizing cell configuration and cathode composition.

Solid-State Cell Configuration



EIS at Open-Circuit

